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Rhodium complexes of 4,5-dicyano-1,2,3-triazole

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Abstract

Neutral bi- and mono-nuclear dicyanotriazolate (DcTz) complexes of formulae $[Rh_2(\mu\text{-DcTz})_2L_2L'_2]$ ($L_2 = L'_2$ = diolefin; L = CO, L′ = PPh_3 or $P(OPh)_3$; L = L′ = $P(OPh)_3$; L_2 = COD, L′ = $P(OPh)_3$) and $[Rh(DcTz)L_2L']$ (L_2 = diolefin, L′ = PPh_3; L = PPh_3, L′ = CO) and the ionic derivative $[Rh(dppe)_2][DcTz]$ have been prepared. New heteroatom-bridged complexes of formula $[Rh_2(\mu\text{-DcTz})(\mu\text{-X})(COD)L_2]$ (L_2 = COD, L = CO) have been obtained by treating $[Rh_2(\mu\text{-DcTz})_2(COD)_2]$ with $[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ (X = Cl), or (X = N_3) by subsequent treatment with NaN_3. The properties of $[Rh_2(\mu\text{-DcTz})(\mu\text{-}N_3)(COD)(CO)_2]$ and the related derivative, $[Rh_2(\mu\text{-DcTz})(\mu\text{-}N_3)(CO)_4]$ indicate the presence of intermolecular interactions. Some oxidative addition reactions of I_2, IMe and $HgCl_2$ to $[Rh_2(\mu\text{-DcTc})_2(CO)_2(PPh_3)_2]$ have been examined.

Introduction

Structure and bonding in rhodium azolate complexes have attracted much interest in recent years [1–13]. Whereas simple pyrazoles act as neutral monodentate ligands coordinating through N(2), pyrazolate type anions generally act as exo-bidentate ligands to form binuclear structures, although monodentate coordination has been observed in a few cases [2b,3]. In contrast, higher nuclearity is observed for related imidazolate bridged complexes [14], but binuclear rhodium(I) triazolate or benzotriazolate complexes are formed [7,9,10], suggesting that the two nitrogen atoms involved in the coordination are adjacent. Furthermore, the presence of uncoordinated nitrogen atoms on the triazolate complexes allows the synthesis of a variety of tri- and tetra-nuclear complexes [7,9,10].

Rasmussen et al. [15,16] have shown that the coordinating ability of the ligands can be influenced by the presence of cyano substituents on the heterocyclic ring. In view of this, we have investigated the coordinating ability of 4,5-dicyano-1,2,3-triazole (HDcTz), which has an acidity similar to that of dichloroacetic acid [17].

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Results and discussion

It has been reported that $[Rh_2(\mu\text{-}Cl)_2(\text{diolefin})_2]$ complexes react with pyrazole or benzotriazole type ligands (Haz) to give mononuclear [RhCl(diolefin)(Haz)] compounds, in which the neutral azole ligand is monodentate. However, binuclear rhodium(I) 4,5-dicyano-1,2,3-triazolate $[Rh_2(\mu\text{-}DcTz)_2(\text{diolefin})_2]$ complexes are obtained by treating $[Rh_2(\mu\text{-}Cl)_2(\text{diolefin})_2]$ with the HDcTz, rather than the expected, neutral species [RhCl(diolefin)(HDcTz)]. The marked acidity of HDcTz accounts for the proton loss [17]. A direct high yield route involves the reaction of [Rh(acac)(diolefin)] with the ligand (eq. 1) (diolefin = 1,5-cyclooctadiene (COD) (I)

$$2\,[Rh(acac)(\text{diolefin})] + 2\,HDcTz \rightarrow [Rh_2(\mu\text{-}DcTz)_2(\text{diolefin})_2] + 2Hacac \qquad (1)$$

or 2,5-norbornadiene (NBD) (II)).

Molecular weight measurements on $[Rh_2(\mu\text{-}DcTz)_2(\text{diolefin})_2]$ complexes show that they are dinuclear, suggesting that the nitrogen atoms of the bridge ligand involved in coordination are adjacent, as found for related triazolate bridged rhodium(I) complexes [7,9]. (See Fig. 1).

The $[Rh_2(\mu\text{-}DcTz)_2(\text{diolefin})_2]$ complexes usually react readily with various ligands. Thus, addition of two moles of triphenylphosphine leads to the cleavage of the dicyanotriazolate bridges and formation of the mononuclear complexes $[Rh(Dctz)(\text{diolefin})(PPh_3)]$ (diolefin = COD (III), NBD (IV)), in which the ligand is monodentate. Complexes III and IV react with carbon monoxide with displacement of the coordinated diolefin and formation of the dinuclear complex $[Rh_2(\mu\text{-}DcTz)_2(CO)_2(PPh_3)_2]$ (V). This complex can also be prepared by bubbling carbon monoxide through a dichloromethane solution of $[Rh_2(\mu\text{-}DcTz)_2(\text{diolefin})_2]$ complexes (presumably with formation of the intermediate $[Rh_2(\mu\text{-}DcTz)_2(CO)_4]$ (ν(CO) (CH_2Cl_2) 2110, 2100, 2050 cm^{-1}) followed by addition of triphenylphosphine. The IR spectrum of complex V shows one terminal metal carbonyl stretching frequency (2010 cm^{-1}), suggesting a *trans*-configuration, in keeping with the *trans*-structure revealed by X-ray diffraction for related pyrazolate complexes [2a]. The ν(CO) bands are shifted by 15–20 cm^{-1} towards higher frequencies in 4,5-dicyano-1,2,3-triazolate compounds relative to those for benzotriazolate compounds [7], in accord with the relatively low σ-donor strength and strong π-accepting properties of the DcTz ligand.

The dicyanotriazolate bridges in complex V can be cleaved by adding triphenyl-

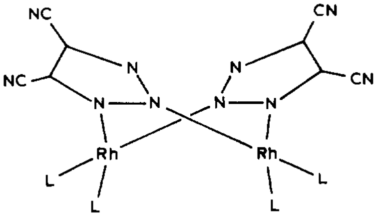


Fig. 1. Proposed structure for dinuclear complexes containing the "$Rh_2(\mu\text{-}DcTz)_2$" framework.

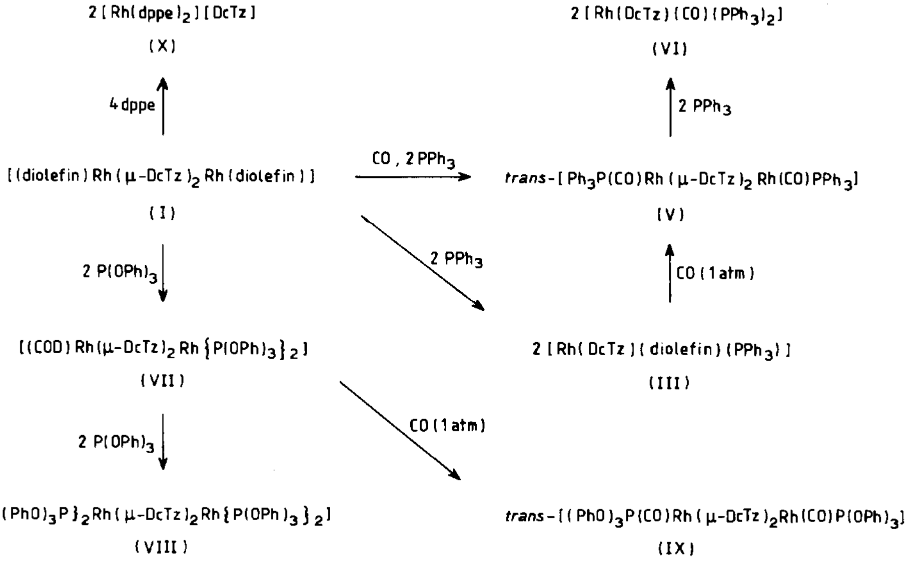
phosphine, leading to formation of the mononuclear complex [Rh(DcTz)(CO)-$(PPh_3)_2$] (VI) *.

Stepwise addition of triphenylphosphite to $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ affords the dinuclear derivatives $[Rh_2(\mu\text{-}DcTz)_2(COD)\{P(OPh)_3\}_2]$ (VII) and $[Rh_2(\mu\text{-}DcTz)_2\{P(OPh)_3\}_4]$ (VIII). Similar results were previously reported for stepwise addition of triphenylphosphite to $[Rh_2(\mu\text{-}X)_2(COD)_2]$ complexes (X = Cl [18] or $X_2 = C_2O_4$ [19]).

The reaction of complex VII with carbon monoxide involves displacement of the coordinated diolefin and formation of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2\{P(OPh)_3\}_2]$ (IX). The presence of a single ν(CO) band (2060 cm^{-1}) suggests a *trans*-configuration, as for complex V.

Reaction of complex I with four moles of dppe gives the anionic compound $[Rh(dppe)_2][DcTz]$, which behaves as 1/1 electrolyte in solution; the cation of this complex is known to be very stable [20]. Table 1 lists the analytical data for the isolated complexes. The various reactions mentioned above are summarized in Scheme 1. The behaviour of the dicyanotriazolate anion may be compared to that of the 3,5-bis(trifluoromethyl)pyrazolate [3]; in both cases the presence of two strongly electron-withdrawing groups facilitate ionization and monodentate coordination, as well as the usual exobidentate coordinate typical of azolate ligands.

The binuclear complex I still has two uncoordinated nitrogen atoms, one from each dicyanotriazolate group, and could thus potentially act as donor centres for the construction of homo- and hetero-tetranuclear complexes, as we have recently observed for benzotriazolate and triazolate ligands [7,21]. Complex I reacts with



Scheme 1

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* The related iridium complexes $[Ir(DcTz)(CO)(PPh_3)_2]$ and $[Ir_2(\mu\text{-}DcTz)_2\{P(OPh)_3\}_4]$ have been obtained from $[Ir_2(\mu\text{-}DcTz)_2(COD)_2]$, by similar methods.

Table 1

Analytical and physical data for the compounds

Complex	Analysis (Found (calcd.) (%))			Yield (%)	Colour	Mol.wt. ($CHCl_3$) found (calcd.)	$\nu(CO)$ (CH_2Cl_2) (cm^{-1})
	C	H	N				
$[Rh_2(\mu\text{-DcTz})_2(COD)_2]$	44.0	3.6	20.9	94	Yellow	665	
(I)	(43.8)	(3.6)	(21.2)			(658)	
$[Rh_2(\mu\text{-DcTz})_2(NBD)_2]$	42.1	2.5	22.2	93	Orange	650	
(II)	(42.2)	(2.5)	(22.3)			(626)	
$[Rh(DcTz)(COD)(PPh_3)]$	61.2	4.3	11.2	81	Yellow	645	
(III)	(60.9)	(4.6)	(11.8)			(591)	
$[Rh(DcTz)(NBD)(PPh_3)]$	60.9	4.0	11.9	77	Orange	605	
(IV)	(60.5)	(4.0)	(12.1)			(575)	
$[Rh_2(\mu\text{-DcTz})_2(CO)_2(PPh_3)_2]$	54.5	3.3	13.7	63	Yellow	920	2010
(V)	(54.0)	(2.9)	(13.7)			(1022)	
$[Rh(DcTz)(CO)(PPh_3)_2]$	62.8	4.0	8.6	72	Yellow		1995
(VI)	(63.6)	(3.9)	(9.0)				
$[Rh_2(\mu\text{-DcTz})_2(COD)\{P(OPh)_3\}_2]$	53.9	3.8	11.4	70	Pale-yellow	1202	
(VII)	(53.3)	(3.6)	(11.9)			(1170)	
$[Rh_2(\mu\text{-DcTz})_2\{P(OPh)_3\}_4]$	57.0	3.5	8.6	69	Yellow	1860	
(VIII)	(57.0)	(3.5)	(8.3)			(1683)	
$[Rh_2(\mu\text{-DcTz})_2(CO)_2\{P(OPh)_3\}_2]$	48.8	3.0	11.9	81	Yellow	1190	2060
(IX)	(49.3)	(2.7)	(12.5)			(1118)	
$[Rh(dppe)_2][DcTz]$	65.8	4.8	6.5	88	Yellow [a]		
(X)	(66.0)	(4.7)	(6.8)				
$[(COD)Rh(\mu\text{-DcTz})(\mu\text{-Cl})Rh(COD)]$	41.6	4.1	12.2	74	Yellow	589	
(XI)	(41.7)	(4.2)	(12.1)			(575)	
$[(COD)Rh(\mu\text{-DcTz})(\mu\text{-Cl})Rh(CO)_2]$	31.9	2.3	13.8	85	Yellow	593	2090,2040
(XII)	(32.1)	(2.3)	(13.4)			(523)	
$[(COD)Rh(\mu\text{-DcTz})(\mu\text{-N}_3)Rh(COD)]$	40.9	4.1	19.3	77	Pale-yellow	602	2040 [b]
(XIII)	(41.2)	(4.1)	(19.2)			(582)	
$[(COD)Rh(\mu\text{-DcTz})(\mu\text{-N}_3)Rh(CO)_2]$	31.0	2.6	20.8	76	Violet		2095,2065, 2035 [b]
(XIV)	(31.7)	(2.3)	(21.1)				
$[(CO)_2Rh(\mu\text{-DcTz})(\mu\text{-N}_3)Rh(CO)_2]$	20.8		23.0	86	Dark-blue		
(XV)	(20.1)		(23.4)				
$[Rh_2(\mu\text{-DcTz})_2I_2(Me)_2(CO)_2\text{-}(PPh_3)_2]$	43.6	3.2	11.1	82	Brown	1401	2095
(XVI)	(44.1)	(2.7)	(10.7)			(1306)	
$[Rh_2(\mu\text{-DcTz})_2I_4(CO)_2(PPh_3)_2]$	36.7	2.2	8.5	88	Brown	1532	2105
(XVII)	(36.1)	(1.9)	(9.1)			(1530)	
$[Rh_2(\mu\text{-DcTz})_2Cl(HgCl)(CO)_2\text{-}(PPh_3)_2]$	42.4	2.3	10.8	88	Red	1307	2090,2010
(XVIII)	(42.6)	(2.3)	(10.8)			(1294)	

[a] Λ_M 85 ohm^{-1} cm^2 mol^{-1} (acetone solution). [b] Azide vibrations are reported together with $\nu(CO)$.

$[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ (L_2 = COD, $(CO)_2$) complexes in acetone to give new hetero-atom-bridged complexes analyzing as $[Rh_2(\mu\text{-DcTz})(\mu\text{-Cl})(COD)(L_2)]$ (L_2 = COD (XI), $(CO)_2$ (XII)); the molecular weight measurements support the dinuclear formulation. The formation of dinuclear complexes may be a consequence of the lower nucleophilicity of the dicyanotriazolate group, which is unfavourable for simultaneous coordination of the three atoms of nitrogen, but steric effects could be

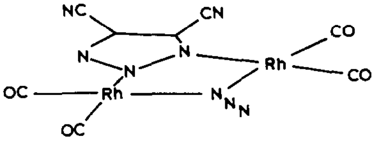

Fig. 2. Hypothesized structure for complex XV.

also important. The reactions of the complexes XI and XII with NaN_3 give the dirhodium complexes $[Rh_2(\mu\text{-DcTz})(\mu\text{-}N_3)(COD)(L_2)]$ (L_2 = COD (XIII), $(CO)_2$ (XIV)) containing both dicyanotriazolate and azide as bridging ligands. Bubbling carbon monoxide through a dichloromethane solution of complex XIV leads to the displacement of the coordinated diolefin (with immediate change in colour from yellow to blue) and this is followed by the precipitation of dark blue solid, which was identified as the complex $[Rh_2(\mu\text{-DcTz})(\mu\text{-}N_3)(CO)_4]$ (XV). Figure 2 shows a suggested structure for complex XV. Interestingly the heterobridged complexes XIV and XV in the solid state exhibit very complex IR spectra in the ν(CO) region. These spectra and the deep blue colours of the isolated complexes indicate the presence of intermolecular interactions. In this context it is relevant to note that we recently structurally characterized a related dinuclear complex showing a stacking arrangement of square planar rhodiums centred along one axis [22].

Some oxidative addition reactions have been studied. Complex V undergoes reactions with iodine or methyl iodide to give complexes of the type $[Rh_2(\mu\text{-DcTz})_2I_2X_2(CO)_2(PPh_3)_2]$ (X = Me (XVI) or I (XVII)). The presence of only a single terminal ν(CO) band in each case, at 2095 and 2105 cm^{-1}, respectively, suggests that single symmetrical dirhodium(III) derivatives were formed. The ν(CO) bands of the oxidation products are shifted towards higher frequencies relative to those for the parent compound. Attempts to isolate the 1/1 adduct $[Rh_2(\mu\text{-DcTz})_2I_2(CO)_2(PPh_3)_2]$ by treating complex V with molecular iodine (1/1 mol ratio) were unsuccessful; only complex XVII and the starting material were isolated. On the other hand, complex V reacts with $HgCl_2$ in 1/1 (or 1/2) mol ratio to give $[Rh_2(\mu\text{-DcTz})_2Cl(HgCl)(CO)_2(PPh_3)_2]$ (XVIII). The appearance of ν(CO) bands at 2090 cm^{-1} (typical of a Rh^{III} centre) and 2010 (typical of a Rh^{I} centre) suggests the presence of a rhodium(III)–rhodium(I) complex, resulting from oxidative addition of $HgCl_2$ to one centre [23,24]; however some increase in the ν(CO) frequency for the carbonyl ligand of the untouched metallic centre would be expected [25] but was not observed in the present case.

Experimental

General procedures. Reactions were carried out at room temperature under air. Solvents were distilled before use. C, H and N analyses were performed with a Perkin–Elmer 240-B microanalyzer. Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer over the range 4000–200 cm^{-1}, with the samples as Nujol mulls or in dichloromethane solutions between NaCl windows; calibration was with polystyrene. Molecular weights were determined with a Knauer vapour pressure osmometer. Conductivities were measured in acetone solutions with a Philips 9501|01 conductimeter.

Starting materials were prepared by published procedures: $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ [26], $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ [27], [Rh(acac)(COD)] [28], [Rh(acac)(NBD)] [28]. 4,5-Dicyano-1,2,3-triazole [29]. Other chemicals were reagent grade, and were used without purification.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (I)

To a solution of [Rh(acac)(COD)] (100 mg, 0.322 mmol) in acetone (20 ml), was added a stoichiometric amount of dicyanotriazole (38 mg, 0.323 mmol). The solution was stirred for 30 min. Concentration under vacuum followed by addition of hexane led to precipitation of the yellow complex, which was filtered off, washed with hexane, and air-dried.

Complex II was similarly prepared starting from [Rh(acac)(NBD)].

Preparation of $[Rh(DcTz)(COD)(PPh_3)]$ (III)

To a solution of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (100 mg, 0.151 mmol) in dichloromethane (20 ml) was added PPh_3 (80 mg, 0.305 mmol). The yellow solution was stirred for 20 min, then the solvent was evaporated off under reduced pressure. Addition of hexane led to the complete precipitation of a yellow solid, which was filtered off, washed with hexane, and air-dried.

Complex IV was similarly prepared starting from $[Rh_2(\mu\text{-}DcTz)_2(NBD)_2]$ and the calculated amount of PPh_3.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2(PPh_3)_2]$ (V)

(i) Carbon monoxide was bubbled through a solution of $[Rh(DcTz)(COD)(PPh_3)]$ (100 mg, 0.133 mmol) in dichloromethane (20 ml) for 15 min. The solution was then evaporated under vacuum, and hexane was added. The solid which separated was filtered off, washed with hexane, and air-dried.

(ii) Carbon monoxide was bubbled through a solution of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (100 mg, 0.151 mmol) in dichloromethane (20 ml) for 15 min to give a pale yellow solution. Addition of solid triphenylphosphine (79.7 mg, 0.303 mmol) caused evolution of carbon monoxide and deepening of the colour. The solution was evaporated under vacuum and hexane was added. The solid which separated was filtered off, washed with hexane, and air-dried.

Preparation of $[Rh(DcTz)(CO)(PPh_3)_2]$ (VI)

To a solution of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2(PPh_3)_2]$ (100 mg, 0.098 mmol) in dichloromethane was added PPh_3 (51.3 mg, 0.195 mmol). The solution was stirred for 30 min, and the solvent then evaporated off under reduced pressure. Addition of ether led to precipitation of a yellow solid, which was filtered off, washed with ether, and air dried.

Preparation of $[(COD)Rh(\mu\text{-}DcTz)_2Rh\{P(OPh)_3\}_2]$ (VII)

$P(OPh)_3$ (79.8 μl, 0.303 mmol) was added to a solution of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (100 mg, 0.151 mmol) in dichloromethane (20 ml). The colour of the solution changed from yellow to pale yellow. After 30 min stirring the solvent was evaporated off under reduced pressure and hexane was added, to give a pale yellow solid, which was filtered off, washed with hexane, and air-dried.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2\{P(OPh)_3\}_4]$ (VIII)

To a solution of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (100 mg, 0.151 mmol) in dichloromethane (20 ml) was added $P(OPh)_3$ (159 μl, 0.600 mmol). This pale yellow solution was stirred for 30 min. Vacuum concentration and addition of ether led to the precipitation of a pale yellow solid, which was filtered off, washed with hexane and air-dried.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2\{P(OPh)_3\}_2]$ (IX)

Carbon monoxide was bubbled for 15 min through a solution of $[(COD)Rh(\mu\text{-}DcTz)_2Rh\{P(OPh)_3\}_2]$ (100 mg, 0.085 mmol) in dichloromethane (20 ml). The solution was evaporated under vacuum and hexane was added. The solid was filtered off, washed with hexane, and air-dried.

Preparation of $[Rh(dppe)_2](DcTz)$ (X)

To a solution of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (100 mg, 0.151 mmol) in dichloromethane (20 ml) was added dppe (242 mg, 0.607 mmol). The solution was stirred for 2 h, then the solvent was evaporated off under reduced pressure. Ether was added, and the yellow solid was filtered off, washed with ether, and air-dried.

Preparation of $[(COD)Rh(\mu\text{-}DcTz)(\mu\text{-}Cl)Rh(COD)]$ (XI)

To a solution of $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ (100 mg, 0.151 mmol) in acetone (20 ml) was added $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (74.8 mg, 0.157 mmol). The solution was stirred for 30 min, then concentrated under vacuum, and hexane was added. The solid was filtered off, washed with hexane, and air dried.

Complex XII was similarly prepared from $[Rh_2(\mu\text{-}DcTz)_2(COD)_2]$ and the calculated amount of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$.

Preparation of $[(COD)Rh(\mu\text{-}DcTz)(\mu\text{-}N_3)Rh(COD)]$ (XIII)

To a suspension of $[(COD)Rh(\mu\text{-}DcTz)(\mu\text{-}Cl)Rh(COD)]$ (174.8 mg, 0.303 mmol) in methanol (20 ml) was added NaN_3 (19.7 mg, 0.303 mmol). The mixture was stirred for 2 h and the suspension then vacuum concentrated to ca. 4 ml and methanol/water (2/1 ml) added. The yellow complex was filtered off, washed with methanol/water (2/1 ml), and air-dried.

Preparation of $[(COD)Rh(\mu\text{-}DcTz)(\mu\text{-}N_3)Rh(CO)_2]$ (XIV)

To a solution of $[(COD)Rh(\mu\text{-}DcTz)(\mu\text{-}Cl)Rh(CO)_2]$ (150 mg, 0.303 mmol) in methanol (20 ml) was added NaN_3 (19.74 mg, 0.303 mmol). The violet complex precipitated spontaneously in almost quantitative yield. The solid was filtered off, washed with methanol/water (2/1 ml) and air-dried.

Preparation of $[(CO)_2Rh(\mu\text{-}Dctz)(\mu\text{-}N_3)Rh(CO)_2]$ (XV)

Bubbling of carbon monoxide through a solution of $[(COD)Rh(\mu\text{-}DcTz)(\mu\text{-}N_3)Rh(CO)_2]$ (100 mg, 0.180 mmol) in dichloromethane (50 ml) for 15 min gave a dark blue solid. The suspension was vacuum-concentrated to ca. 4 ml and hexane was added. The solid was filtered off, washed with hexane, and air-dried.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2I_2Me_2(CO)_2(PPh_3)_2]$ (XVI)

A solution of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2(PPh_3)_2]$ (100 mg, 0.097 mmol) in 30 ml of methyl iodide was stirred for 4 days. The solution was concentrated to 2 ml under reduced pressure, and hexane then added, to give a brown solid, which was filtered off, washed with hexane, and air-dried.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2I_4(CO)_2(PPh_3)_2]$ *(XVII)*

To a solution of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2(PPh_3)_2]$ (100 mg, 0.097 mmol) in 20 ml of dichloromethane was added a stoichiometric amount of iodine (49.6 mg, 0.195 mmol). The colour of the solution changed from yellow to brown. The progress of the reaction was monitored by IR spectroscopy, and after 30 min stirring the solvent was evaporated off and hexane was added to give a dark brown solid. This was filtered off, washed with hexane, and air-dried.

Preparation of $[Rh_2(\mu\text{-}DcTz)_2Cl(HgCl)(CO)_2(PPh_3)_2]$ *(XVIII)*

Addition of $HgCl_2$ (26.5 mg, 0.097 mmol) to a solution of $[Rh_2(\mu\text{-}DcTz)_2(CO)_2(PPh_3)_2]$ (100 mg, 0.097 mmol) in 20 ml of dichloromethane caused a change from yellow to red. The solution was stirred for 30 min, then the solvent was evaporated off under reduced pressure. Addition of hexane give a red solid, which was filtered off, washed with hexane, and air-dried.

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